

Report Documentation Page			Form Approved OMB No. 0704-0188	
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1. REPORT DATE 2005	2. REPORT TYPE	3. DATES COVERED 00-00-2005 to 00-00-2005		
Cavitands: Containers Molecules for Surface Plasmon Resonance (SPR)-Based Chemical Vapor Detection			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Center for Bio/Molecular Science and Engineering, 4555 Overlook Avenue SW, Washington, DC, 20375			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 3
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified		

CAVITANDS: CONTAINER MOLECULES FOR SURFACE PLASMON RESONANCE (SPR)-BASED CHEMICAL VAPOR DETECTION

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Introduction: Hazardous chemical vapors pose a serious challenge to the security and well-being of our nation and to our forces abroad. These can be dangerous chemical warfare agents (CWAs) and explosives or health hazards such as toxic industrial chemicals and materials (TICs and TIMs). A long-standing problem with chemical vapor detectors is their susceptibility to false alarms, which results in disruption of normal activities. In detectors that use a chemically sensitive coating layer, such false alarms are caused by inadequate selectivity toward target molecules. Therefore, there is a critical need to develop novel chemical coatings that can enhance selectivity of detection for specific targets or analytes. Cavitands solve this problem by enhancing the selectivity of detection towards chemical vapors.

Cavitands: Inspired by the exquisite specificity of biomolecules such as antibodies for target antigens, supramolecular chemistry is attempting to do the same for small molecule targets through the use of synthetic receptors called cavitands.¹ These molecules have the potential to be selective, because of their unique biomimetic nanostructures. Cavitands derive their name from the shape of their cavities (Fig. 6). These molecules are designed to bind target molecules to form guest-host complexes. By tuning the cavity depth, shape, and chemical functionality that controls the synergistic interactions with analyte molecules, cavitands for a range of molecular targets may be designed and synthesized. This strategy for selectivity-enhancement is fundamentally different from that used in other chemically selective coatings (for example, polymers) that rely on the solubility of the targets with the coating layer.

Although target molecules may bind selectively to such tailored cavitand molecules, it is equally important to transduce the binding event by using an appropriate technique that has high sensitivity. We show that, by using a real-time, label-free, optical technique called surface plasmon resonance (SPR, see Fig. 7), refractive index changes induced by analyte-cavitand interactions provide selective signals for sensitive chemical vapor detection.

Cavitands are evaluated at NRL through a collaboration with Professor Enrico Dalcanale at the University of Parma, Italy. Three cavitands named MeCav (for methylene-bridged), PzCav (pyrazine-bridged), and QxCav (quinoxalines-bridged) were chosen to demonstrate selectivity toward aromatic vapors. The presence of alkyl tails (R) at the bottom of the cavity is to make them soluble in common solvents such as chloroform. Cavitand solutions (0.38 mM) in chloroform were spin coated onto surface plasmon resonance substrates (50-nm thick gold-coated cover glass). Spin coating was performed at 4000 rpm for 60 s at room temperature. The spin coating parameters gave a film thickness (confirmed using spectroscopic ellipsometry) of nearly 4 nm. For targets, a variety of analyte vapors belonging to different chemical classes were studied. QxCav with the deepest cavity was designed to form guest-host complexes with aromatic vapors, whereas cavitands with shallower cavities (such as MeCav and PzCav) were not expected to be as selective toward such guest molecules.

Surface Plasmon Resonance (SPR): An SPR experimental set up based on the Kretschmann configuration (Fig. 7) was used for all the measurements. The glass prism, made of standard BK7 glass (refractive index $n = 1.5$, Howard Jonson Optical Laboratories), was index matched to the gold-coated cover glass that was used as the sample substrate ($n = 1.51$) using an index-matching liquid from Cargille Inc. The thickness of the gold film was nominally 50 nm, and it had an underlying chromium adhesion layer of about 2-nm thickness. A 635-nm diode laser (Lasermax, Inc.) was used as the light source. A Glan Thompson linear polarizer (Karl Lambrecht, Inc.) was placed in the path of the light beam to ensure that only *p*-polarized light (surface plasmons are excited by *p*-polarized light) was incident on the glass prism. The reflected light was monitored using a photodiode (818 Series, Newport Corporation) calibrated for the chosen wavelength. Variable angles were selected by means of a stepper-motor-controlled goniometer with an angular resolution of 0.01 deg. The experimental data acquisition system was computer-controlled, with a typical angular scan (from 40 to 80 deg) taking about 8 min.

SPR Shifts: Figure 8 shows surface plasmon angle shifts observed due to three different cavitands that were spin-coated onto three separate SPR substrates. The red curve with the smallest plasmon angle minimum (~ 46 deg) is that from a bare gold substrate with no cavitand coated; successively higher shifts were

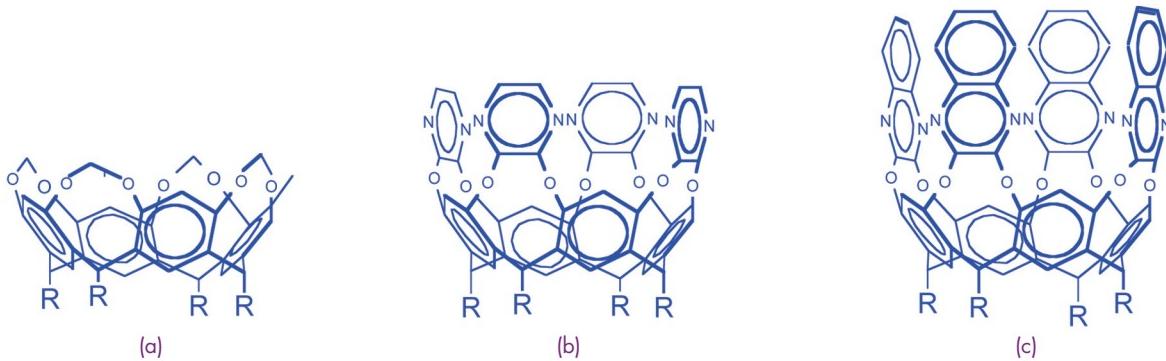


FIGURE 6

Three cavitands: (a) MeCav (methylene-bridged), (b) PzCav (pyrazine-bridged), and (c) QxCav (quinoxalines-bridged) with varying depths and therefore complexing ability with target molecule.

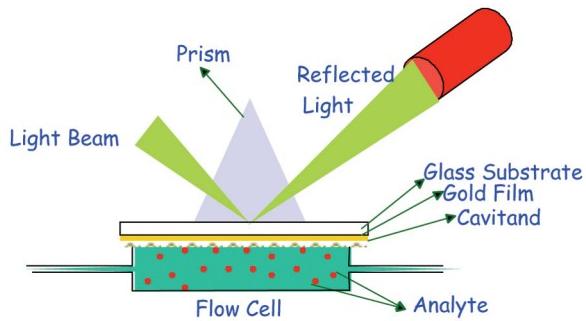


FIGURE 7

The surface plasmon resonance (SPR) experimental arrangement using angular interrogation.

obtained due to MeCav, PzCav, and QxCav coated substrates, respectively. It is observed (see Fig. 6) that the presence of polarizable groups on the molecules causes a larger shift of the plasmon angle (plasmon angle increase follows the sequence QxCAv > PzCAv > MeCav). These baseline shifts were subtracted from the signal due to interaction of cavitands with analyte vapors.

Cavitand Selectivity toward Chemical Vapors:

Figure 9 shows the plasmon angle shifts due to the interaction of various target analytes belonging to vapors of different chemical classes (ethyl acetate, dichloromethane, acetonitrile, toluene, and benzene) with the three different cavitands. For comparison of the selectivity of the cavitands with other sensing layers, we carried out similar experiments with polymer-coated layers. Specifically, the signals obtained due to exposure of the same vapors with two polymer coatings, polyepicholorhydrin (PECH) and polyisobutylene (PIB), were compared. These specific polymer coatings have been demonstrated in the past to show selective response toward aromatic vapors. Figure 9 shows that, for a given concentration of the vapors (100 ppm), the polymer sensing layers do not

generate an observable signal. This is despite the fact that the polymer films were about twice as thick as the cavitand films obtained under identical spin-coating conditions. This clearly demonstrates the higher selectivity of the cavitands.

As pointed out earlier, the depth of the cavitands plays a role in selectivity. MeCav, with a shallow cavity, shows hardly any response toward the aromatic vapors, while PzCav, with a slightly deeper cavity, shows a signal well above baseline. However, QxCav, with the deepest cavity, shows the largest SPR signal response toward the aromatic vapors, benzene and toluene.² Clearly therefore, the enhancement in selectivity due to the size and shape of the cavities plays an important role in enhancing the signal due to the cavitand-analyte interactions. Figure 9 shows a pattern of response to several analytes using the cavitand and polymer sensing films. Such patterns may be used with pattern recognition algorithms to identify known and possibly unknown analytes. This has the additional advantage of higher signal response due to the high selectivity of cavitands. We have also recently shown that the morphology of the cavitand-coated film does not influence the selectivity.³ This will allow simple industrial processes to be used for coating cavitand films onto sensor surfaces.

The interaction forces that stabilize the guest-host complexes (between cavitand and target analyte) are noncovalent in nature. This allows us to recycle the cavitands in a sensor and can be accomplished either by raising the temperature of the coating layer or forcing a stream of nitrogen gas over it. An important feature of the cavitands is that they are highly robust, synthetic receptors. This allows them to be integrated into rugged detectors.

Conclusions: Cavitands have been shown to be highly promising as supramolecular nanostructures for the selective complexation of chemical vapors. This

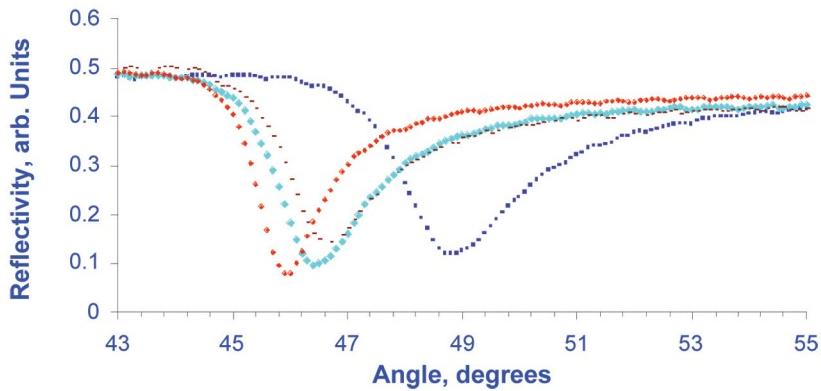


FIGURE 8

Minima in each of the raw data curves corresponds to the surface plasmon angle. The plasmon angle minima starting from left to right are for (a) bare gold, (b) MeCav-coated substrate, (c) PzCav-coated substrate, and (d) for QxCav-coated substrate.

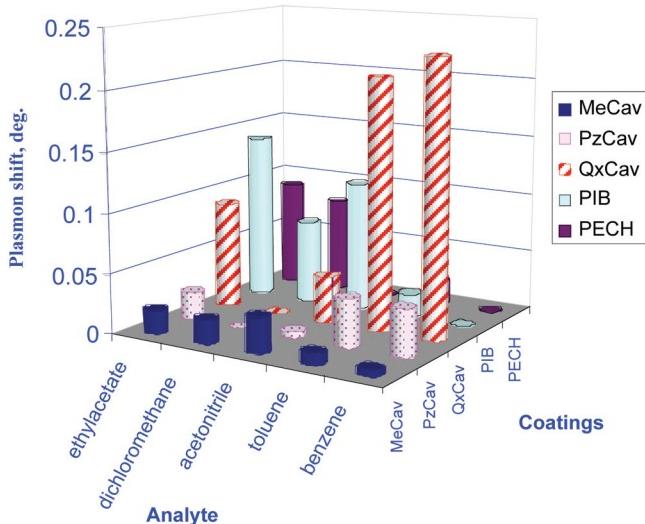


FIGURE 9

Selectivity patterns observed for different chemical vapors using the three cavitands, MeCav, PzCav, and QxCav. The comparison is for a fixed concentration of 100 ppm for all vapors. Also shown for comparison are the results for the polymer coatings, PECH and PIB. The quinoxalines-bridged cavitand molecules, QxCav, are highly selective toward aromatic vapors due to the complementary cavity size and interactions.

selectivity arises due to the size, shape, and interaction complementarity between the target analyte and cavitands. The methylene-bridged cavitands (MeCav) with shallow cavities do not complex aromatic vapors, the pyrazine-bridged cavitands (PzCav) show intermediate selectivity, whereas the quinoxalines-bridged cavitands (QxCav) with the deepest cavities show the best selectivity for aromatic vapors. A comparison with polymer coatings, PECH and PIB, shows that cavitands have higher selectivity despite the fact that the polymer coatings are more than twice the thickness of the spin-coated cavitand films. Combined with the fact that cavitands are robust synthetic receptors, they are promising materials for the selective detection of hazardous chemical vapors. We have recently shown that a new SPR system based on wavelength interrogation with real-time detection capabilities can be used to obtain sub-ppb sensitivity to DMMP (sarin simulant) vapors. The next challenge is to demonstrate the selectivity of cavitands in real-world environments

where interferents are present. We expect the high selectivity of cavitands to significantly reduce the false alarm rate in future chemical detectors.

Acknowledgments: I wish to acknowledge Dr. E. Feresenbet, my former NRC Research Associate, Prof. E. Dalcanale at the University of Parma, Italy, and Dr. C. Dulcey at NRL for the SPR set up.

[Sponsored by ONR and the Joint Services NMCBD Program]

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